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Monolayer Deposition of Bisphenol A Polycarbonate Oligomers on Au(111)

René Gustus^{a,c}, Lienhard Wegewitz^{b,a}, Sascha Sedelmeier^d, Oliver Höfft^c,
Jürgen Wieser^d, Matthias Rehahn^d, Frank Endres^c and Wolfgang Maus-Friedrichs^{a,c,*}

^a *Institut für Energieforschung und Physikalische Technologien, Technische Universität
Clausthal, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany*

^b *Clausthaler Zentrum für Materialtechnik, Technische Universität Clausthal, Leibnizstrasse
4, 38678 Clausthal-Zellerfeld, Germany*

^c *Institut für Elektrochemie, Technische Universität Clausthal, Arnold-Sommerfeld-Straße 6,
38678 Clausthal-Zellerfeld, Germany*

^d *Fraunhofer-Institut für Betriebsfestigkeit und Systemzuverlässigkeit LBF, Schloßgartenstr. 6,
64289 Darmstadt, Germany*

* Corresponding author: w.maus-friedrichs@pe.tu-clausthal.de

Abstract

The deposition behavior of bisphenol A polycarbonate (BPA-PC) on a Au(111) single crystal has been studied. Thin films of PC were prepared by in-situ evaporation of PC pellets under UHV conditions. The resulting PC/Au(111) interfaces were characterized by means of Ultraviolet Photoelectron Spectroscopy (UPS), X-Ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). XPS and UPS revealed that no decomposition of the polymer takes place during evaporation. The C1s and O1s XPS core level analysis as well as the UPS spectra show distinct features which can be attributed to chemical bonding states of the PC molecule. Therefore we conclude that the molecular structure within the monomeric unit remains intact after evaporation. Furthermore STM measurements in the submonolayer regime revealed a self-assembly of small polymer chains of 2-4 monomeric units on the Au(111) surface.

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3 **Keywords:** bisphenol A polycarbonate, Au(111) surface, self-assembly, x-ray
4 photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, scanning tunneling
5 microscopy
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15 Due to some of their unique and unusual properties, synthetic polymers like
16 Polyethylene (PE), Polyvinylchloride (PVC) or Polycarbonate (PC) provide one of the most
17 important fields of chemical industry. The chemical and technical properties can be
18 specifically adjusted in a wide range, for example by the choice of the production process or
19 by the admixture of specific additives. A huge industrial branch arose, which deals with the
20 production and processing of polymers. The possible applications are manifold and can be
21 found in our everyday life. Nevertheless polymers are also in the focus of scientific research.
22 Among others, polymer/metal interfaces has become of great interest due to their possible
23 applications in micro- and optoelectronic devices.^{1,2} In this regard the adhesion between
24 polymer and metal is of particular importance. Whereas in this case a distinct linking between
25 polymer molecules and a metal surface is preferable, a strong adhesion can also be a problem,
26 especially during the molding of plastic components. Typical effects due to the contact
27 between a flowing polymer melt and a metal surface are the formation of deposits and strong
28 abrasive forces.
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39 However, in many cases there is a lack of fundamental understanding of the adhesion
40 and the underlying mechanisms concerning the interaction between polymers and metals. In
41 principle there are three different types of adhesion: (i) mechanical, (ii) physical and (iii)
42 chemical adhesion.³ The mechanical adhesion depends essentially on the topographic nature
43 of the surface. Long range physical forces originating from Van-der-Waals or dipol-dipol
44 interactions are responsible for a physical adhesion. The strongest adhesive force related to a
45 direct interaction between polymer molecule and the metal surface is chemical bonding. The
46 way how the polymer interacts with the surface strongly depends on the metal and on the
47 polymer itself. The chemical structure of the polymer on the one side and the electronic
48 structure of the metal surface on the other side are crucial for the interaction. The geometrical
49 arrangement of the polymer molecules is further closely related to the adsorption process. The
50 common idea about the adsorption of polymers to metal surfaces assumes that the molecules
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3 interact only with their chain ends.³ This means that either both ends or just one end adsorb to
4 the surface, whereas the remaining part of the polymer is oriented apart from the surface.
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7 Theoretical and especially experimental studies according this topic can only be found
8 for some polymer metal combinations and are often restricted to adsorption studies of the
9 monomer on well defined surfaces. Fischer et al. studied the adsorption of Bisphenol A (BPA)
10 on Cu(111), which is the monomer of PC and basically consists of two phenol rings linked by
11 an isopropylidene group.⁴ They found a variety of configurations of the molecule on the
12 Cu(111) surface depending on the annealing temperature. In addition chemical analysis
13 revealed a temperature-induced deprotonation of the molecule. For all ordered phases DFT
14 calculations predicted the BPA molecule being adsorbed with one phenol ring parallel to the
15 substrate and the other one tilted and pointing away from the surface. The self-assembly is
16 further proposed to be arising from intermolecular hydrogen bonding between the BPA
17 molecules.
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20 In the case of polycarbonate, Delle Site et al. studied the interaction of Bisphenol A
21 polycarbonate (BPA-PC) molecules with a Ni(111) surface by DFT calculations.⁵ They found
22 strong chemisorption of the phenoxy end groups to Ni(111). Furthermore they suggest that
23 only these chain ends of the polymer adsorb to the metal surface in the case of a perfect defect
24 free surface.
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27 Experimental results concerning the interaction of polycarbonate with metal surfaces
28 are rare. To get an experimental insight into the origin of the adsorption and adhesion of
29 polymers like PC on metal surfaces, thin and defined polymer/metal interfaces have to be
30 prepared. In this work we investigated the deposition of PC on Au(111). Thin films of PC
31 were prepared in-situ by evaporation onto the clean Au(111) surface and were subsequently
32 analyzed by means of X-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron
33 Spectroscopy (UPS) and Scanning Tunneling Microscopy (STM). With this study we tried to
34 work out a reliable procedure to prepare thin PC films on different metal surfaces and to
35 investigate the adsorption of PC on metal surfaces by means of studying the PC/Au(111)
36 interface as a model system.
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Results and Discussion

Core level and valence band spectroscopy (XPS and UPS)

For the interpretation of our XPS and UPS spectra of the thin PC films evaporated on the Au(111) surface the reader is referred to Figure 1, where the monomeric unit of PC is shown. The monomer contains different carbon and oxygen species: 1) aromatic carbon, 2) aliphatic carbon, 3) C_{arom.}-O, 4) O=C=O, i) O=C and ii) C_{arom.}-O-C. These chemical species and their proportional amount are characteristic for the intact structure of the polymer. If a systematic cracking of chemical bonds within the polymer chains would occur during evaporation or due to surface induced chemical reactions, a change in these characteristic properties should occur.

The XPS C1s and O1s detail core level spectra of a PC film evaporated on Au(111) with a thickness of 3 nm are shown in Figure 2. The C1s spectrum can be fitted very well with four peaks (1-4) at binding energies of 284.5 eV, 285.0 eV, 286.2 eV and 290.4 eV, corresponding to aromatic carbon, aliphatic carbon, C_{arom.}-O and O=C=O respectively.⁶ Two additional peaks (5, 6), showing up as a high energy shoulder at binding energies of 291.3 eV and 292.5 eV, can be attributed to the π - π^* shake up emission of the aromatic carbon. The deconvoluted O1s spectrum contains two peaks at binding energies of 532.3 eV and 533.9 eV, which can be assigned to O=C and C_{arom.}-O-C, respectively.⁶ The deconvolution of the C1s and O1s spectra are so far, in good agreement with the chemical structure of the polymer as shown above and with other works dealing with the XPS analysis of PC.^{6,7,8} Nevertheless there is one additional peak, marked with (*), in the C1s spectrum at about 288.0 eV which cannot be directly assigned to PC. This peak can be most likely attributed to O-C-O and C=O, respectively.⁸ These species might be a result of chemical modifications of some of the carboxyl groups in between the polymer. If we consider that the polymer chains do have a finite length, these species might also originate from the cracking of some polymer chains due to decarbonylation of carboxyl groups.

Figure 3 shows UPS He I valence band spectra of PC on Au(111) as a function of PC coverage. The features in the spectrum of the clean Au(111) surface (dashed line) at binding energies of 2.6 eV, 4.1 eV, 4.7 eV, 6.0 eV and 6.9 eV (II-VI) can be attributed to the Au5d emission, the broad plateau near the Fermi edge (I) can be further assigned to emission from the Au s-p band.⁹ After deposition of 0.2 nm of PC (0.2 nm equals to approx. 0.5 ML, where

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3 1 ML corresponds to the complete adsorbate coverage of the surface) the Au(111) specific
4 structures decrease, while a new feature appears at a binding energy of 9.5 eV (D).
5 Considering quantum-chemical calculations concerning the electronic band structure of PC by
6 Moliton et al. we attribute the origin of this peak to C=O and a mixture of O2p and C2p
7 orbitals with emphasis to the O2p emission.¹⁰ Further deposition of PC is accompanied by a
8 small shift of this peak of 0.2 eV towards lower binding energy. In addition a second feature
9 arises at about 3.9 eV (A), superimposing the emission of the Au5d band (III), which is
10 derived most probably from the C2p band and the π -Orbitals of the phenyl rings,
11 respectively.¹⁰ At coverages above 1 nm of PC the peak at 6.0 eV (V) does not further
12 decrease and a new feature at a binding energy of 6.3 eV appears (B), originating from C2p
13 and O2p emission.¹⁰ Additionally two more structures arise at binding energies of 7.9 eV (C)
14 and 12.6 eV (E). The first one can be assigned to emission from the C2p band and phenyl
15 groups.¹⁰ The peak at the high energy side derived most probably from a combination of C2s,
16 C2p and phenyl groups.¹⁰
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27 Both the deconvolution of the C1s and O1s core level spectra and the analysis of the
28 UPS spectra show that characteristic features of the polymer, such as chemical bonds and
29 specific functional groups, seems to be present and intact. The π - π^* shake up emission of the
30 aromatic carbon in the C1s spectrum as well as specific features in the UPS spectra,
31 corresponding to the phenyl rings, (A,C,E) indicate the presence of aromatic carbon within an
32 intact aromatic ring system. Furthermore the C1s spectrum clearly shows the existence of
33 O=C=O bonds (4), which are distinctive for the carboxyl group within the PC molecule. As it
34 is evident from the UPS spectra, there is no significant peak shift as a function of PC
35 coverage, which indicates a weak interaction between the adsorbate and the substrate. Table 1
36 summarizes the relative amounts of the different C1s and O1s species derived from the
37 experiments compared to the theoretical values of the polymer. It shows that the composition
38 of the thin film evaporated on the Au(111) surface is in good agreement with the composition
39 of the PC polymer.
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49 The XPS and UPS results suggest that the molecular and chemical structure within the
50 monomeric unit is still intact. However it is not possible to make any assumption about the
51 actual length of the polymer-chains by means of XPS and UPS. In principle it is possible that
52 the prepared film does not consists of long intact chains, but is composed of small PC units,
53 or oligomers, of different length, down to monomers. The chemical and structural integrity of
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3 the polymer-chains depend primarily on the evaporation process. With increasing temperature
4 the probability for degradation and decomposition of the polymer increase. The probability
5 for evaporation on the other hand is a function of the chain length and is more likely for
6 shorter chains. A lot of work has been done, over the last decades by several groups, dealing
7 with the degradation and decomposition of polycarbonate in different atmospheres and in
8 vacuum.^{11,12,13,14,15} It becomes apparent, that these processes can proceed over different
9 pathways: hydrogen cleavage, bond scission, hydrolysis, alcoholises, leading to different
10 degradation products like CO₂, various phenol structures, carbonates and bisphenol A, to
11 name only a few. However the main degradation and decomposition region is observed at
12 temperatures beyond 500 K between 770 – 970 K. Below these temperatures a significant
13 degradation or decomposition of PC has not been observed. Nevertheless these processes
14 cannot be neglected even though we assume that degradation and particularly decomposition
15 do not play a major role during evaporation of PC at 500 K. In this regard Vree *et al.* studied
16 the preparation of thick PC films by evaporation of PC pellets at 570 K under vacuum
17 conditions.¹⁶ Besides the structure and morphology of the films, they also focus on the
18 evaporation mechanism and the involved degradation and decomposition processes. Using
19 infrared spectroscopy they were able to prove that the bonding structure of the polymer
20 remains intact. However mass spectroscopy measurements during evaporation showed, that
21 the molecular weight and the chain length of the polymer are reduced. Different types of
22 oligomers between monomer and heptamer can be found which are referred to chain-scission
23 during thermal annealing. Larger chains cannot be excluded, but were not detectable due to
24 technical limitations. The authors conclude that during evaporation no decomposition or
25 cross-linking of the polymer take place and that the prepared films consists of oligomeric
26 polycarbonate.

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29 All these things considered, let us assume, that the molecular and chemical structure
30 within the monomeric unit remains intact and that no decomposition takes place during
31 evaporation at 500 K. This is consistent with our XPS and UPS measurements. The actual
32 structure of the adsorbed molecules is still unclear and cannot be determined by means of
33 XPS and UPS.
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Scanning Tunneling Microscopy (STM)

The deposition of PC on Au(111) in the sub-monolayer range, as it is depicted in the RT-STM images in Figure 4, results in the formation of flat islands, which consist of a well-defined arrangement of chain-like structures. In-between these islands some small dark spots can be seen (Figure 4a), originating most probably from carbon or oxygen impurities, adsorbed on the surface during the deposition process. The islands are well-defined and no amorphous phases, especially at the boundaries or in-between the islands, are visible. Besides no adsorption at the step edges can be seen. The herringbone superstructure for the clean Au(111) surface, as it is shown in the inset of Figure 4a, is clearly visible, even straight through the islands. As shown in Figure 4b, the orientation of the islands seems to be arbitrary. No preferential arrangement relative to the herringbone superstructure or to step edges can be identified. This is also the case for other areas of the surface, which are not shown here. However we are not able to make a reliable statement about preferential orientations or arrangements of the islands, this could be the task for further investigations.

To get a closer look into the molecular arrangement of the adsorbed phase, Figure 5 provides high resolution STM images of different islands. Depending on the scan direction with respect to the island orientation (highlighted by white lines in Figure 5a and c), the molecular structures appear slightly different. In Figure 5a and b the island is oriented nearly along the scan direction. STM shows a complex arrangement of bright and spherical protrusions which exhibit a periodic structure perpendicular to the island orientation. The distance between similar molecular features amounts to 5 nm. In Figure 5c and d STM was performed with the scan direction nearly perpendicular to the island orientation. In this case the bright protrusions appear to form small and angled chains which show a distinct arrangement. To illustrate this, Figure 6a contains an overlay of a corresponding simple ball and stick model on the structures seen in the STM image of Figure 5d. The chains are arranged in a point-symmetric alternating fashion perpendicular to the island orientation. The periodicity of similar chains amounts to 5 nm. In Figure 6b this model is transferred to the structures observed in the STM image of Figure 5b. Although the molecular arrangements appear different, this model fits the structures very well.

According to Figure 6c the size of one angled chain is about 2.4 nm, whereas the entire length of one chain segment amounts to 3.5 nm. The theoretical size of the PC monomer is about 1.4 nm supposing a flat geometry (calculated using the molecule editor

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3 Avogadro). If we consider that segments of PC do not show a completely flat adsorption, as
4 it is predicted in an extrem scenario by Delle *et al.* for long PC chains on a perfectly flat
5 Ni(111) surface, where the adsorption is mediated only by phenoxy end groups, the size of the
6 monomer might be somewhat smaller, probably about 1 nm.⁵ (The size of the geometry
7 optimized PC monomer using Avogadro amounts to 1.1 nm). As a matter of fact, these values
8 may not be very accurate and cannot compete with expensive DFT calculations. However
9 they are sufficient enough to get an idea about the molecular structure of these chain
10 segments. Considering an entire chain length of 3.5 nm the corresponding segment would
11 consist of 2.5 to 3.5 monomeric units.
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19 Now the question arises whether these small chains actually represent segments of PC
20 and whether these may be part of long PC chains adsorbed next to each other. First of all a
21 decomposition and fragmentation of the polymer into sub-monomer units such like phenol
22 and carboxyl groups during evaporation can be excluded. Our XPS and UPS measurements of
23 thin PC films and the corresponding remarks about the decomposition and degradation of PC
24 during thermal annealing makes it a priori reasonable to presume that the prepared films
25 consists of small chains of PC. However the low evaporation temperatures result in two
26 contrary effects. On the one hand, decomposition and degradation of the polymer do not play
27 a major role during the evaporation process. On the other hand, the probability for
28 evaporation is indeed a function of chain length at a given temperature and is more likely for
29 short chains. Therefore we assume that the prepared films consists of small PC molecules of
30 about 2-4 monomeric units, as it is depicted in the STM images of Figure 6. These small PC
31 segments either still being part of the source material or have been generated by chain
32 scission during thermal annealing.
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43 It appears that only this PC species is evaporated, which indicates a significant
44 influence of the annealing temperature on the evaporation probability, and that the islands are
45 held together by intermolecular forces. These assumptions are confirmed by several facts
46 derived from the STM measurements: i) Besides the well arranged islands, no other phases
47 like an amorphous phase of molecules in- between or at the boundaries of the islands can be
48 seen. These areas predominantly show the clean Au(111) surface with its characteristic
49 herringbone superstructure. ii) No adsorption at step edges is visible. iii) All islands exhibit
50 the same periodic structure. iv) There are no domains within the islands showing a different
51 arrangement of molecules. According to the dissociation energies of specific bonding species
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3 within the PC, as depicted in Fig 7, the small PC molecules do not have to consist of integral
4 units of the monomer.¹⁵ Due to quite similar dissociation energies along the chain-
5 connections, in principle different endgroups are possible.
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9 Furthermore we assume that the PC molecules do not adsorb completely flat on the
10 Au(111) surface. In a recent work about the adsorption and self-assembly of bisphenol A
11 (BPA) on Cu(111) S. Fischer *et al.* showed that the BPA molecule adsorbs with one
12 phenylene ring lying flat on the surface and the other pointing towards the vacuum.⁴ In
13 addition DFT calculations of crystalline analogs of PC revealed angled molecules of different
14 geometrical conformations.^{17,18,19} In all these cases the molecules show an angled and tilted
15 conformation, similar to our results, particularly along the phenylene – isopropylidene –
16 phenylene bonding. The fact that the herringbone superstructure of the Au(111) surface is
17 clearly visible even beneath the islands further indicates, that there is only a weak interaction
18 (*e.g.* Van-der-Waals), between the PC molecules and the substrate. This is in good agreement
19 with our UPS measurements and with other works dealing with the adsorption of related
20 molecules, for example the adsorption of diphenyl-carbonate on Ag(111).²⁰ In addition
21 Blomqvist *et al.*, who studied the adsorption of segments of bisphenol A polycarbonate on
22 Al₂O₃, pointed out that Van-der-Waals interaction is in principal responsible for the adhesion
23 process of BPA-PC.²¹ They also showed that the segment consisting of two phenylene groups
24 linked by isopropylidene adsorb with one phenylene ring nearly flat to the surface and the
25 other one pointing away from the surface, which is consistent with the results for BPA on
26 Cu(111),⁴ whereas other segments like the carbonate group which is surrounded by two
27 phenylene groups show a nearly flat adsorption configuration, with the carbonate group
28 attaching the surface.
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42 Considering all this we can assume that the PC molecules adsorb to the surface with
43 parts of the molecule lying nearly flat to the surface (phenylene-carbonate-phenylene groups)
44 and other ones pointing upwards (phenylene-isopropylidene-phenylene groups) and being
45 tilted, forming an angled adsorption structure.
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Summary and Conclusions

To study the physical and chemical interaction of polymers like polycarbonate (PC) with metal surfaces, detailed investigations of the interface polymer/metal are crucial. Therefore a method to prepare thin and well defined polymer/metal interfaces is required. In this work we studied the deposition of bisphenol A polycarbonate on Au(111), by in-situ evaporation of PC pellets at 500 K. The thin films were characterized by means of Ultraviolet Photoelectron Spectroscopy (UPS), X-Ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). UPS and XPS showed that the thin polymer films exhibit a distinct bonding configuration, which can be clearly assigned to the chemical structure of PC. A decomposition of the polymer during the evaporation process can be excluded. STM measurements of submonolayers of PC evaporated on the Au(111) surface revealed a complex adsorption structure. The adsorbed phase quite likely consists of small PC chains of 2-4 monomeric units. Hence the evaporation of PC at 500 K is suitable to prepare thin molecular films of oligomeric PC.

Methods

The sample preparation and the spectroscopic measurements were carried out in an Ultra High Vacuum (UHV) apparatus (OMICRON Multiprobe System) with a base pressure of 5×10^{-11} mbar, equipped with several devices for sample cleaning, preparation and analysis. The Au(111) sample (Mateck) was mounted on a molybdenum sample plate and was transferred into the UHV by a three stage transfer system. The clean Au(111) surface was prepared by cycles of Ar^+ ion sputtering at 1 kV, using a commercial ion gun (ISE 5, Omicron) and subsequent annealing up to 800 K by radiative heating. The preparation of the clean Au(111) surface was validated by means of XPS, UPS and STM.

Thin films of PC were prepared in-situ by melting and evaporation of polycarbonate pellets (Makrolon®, Bayer Material Science AG) at 500 K using a molecular evaporator (TCE-BSC, Kentax). The PC was previously outgassed at 370 K for at least 1 hour and at 470 K for several minutes. The distance between sample and molecular evaporator amounted to 1 cm. The deposition rate at these parameters was previously determined with the help of XPS

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3 to be 0.6 nm/minute. The background pressure during evaporation was better than 2×10^{-9}
4 mbar.
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7 XPS was performed with a non-monochromatic X-Ray source (DAR 400, Omicron)
8 using the AlK α line (1486.6 eV). UPS measurements were done with the He I line (21.2 eV)
9 of a standard VUV source (HIS 13, Omicron). For both techniques a hemispherical analyzer
10 (EA125, Omicron) with a pass energy of 10 eV for XPS and 5 eV for UPS, mounted 45° to
11 the surface normal, was used. Qualitative and quantitative analysis of the XPS spectra were
12 performed using CasaXPS as well as Origin7G. For peak fitting the Levenberg-Marquardt
13 algorithm was applied using a linear background subtraction for the C1s and O1s core level
14 spectra. All XPS spectra are further charge corrected to the aromatic carbon in the C1s with a
15 binding energy of 284.5 eV.
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18 STM measurements were performed using a variable temperature STM/AFM (VT-
19 STM/AFM, Omicron) which is part of the UHV apparatus described above. STM tips were
20 prepared ex-situ by electrochemical etching of Tungsten wires (0.2 mm diameter) in a NaOH
21 solution. The STM tips were subsequently heated in-situ by electron bombardment up to 1300
22 K using a home-build device for STM tip conditioning, to remove residual oxide layers and
23 contaminants from the etching solution.
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26 The deposition procedure as well as XPS, UPS and STM measurements were
27 performed with the Au(111) substrate being at room temperature.
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30 31 32 33 34 35 36 37 38 **Acknowledgements**

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40 The authors would like to thank Bayer Material Science AG for providing the polycarbonate.
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Tables

	C1s					O1s	
	C-C arom.	C-C aliph.	C _{arom.} -O	O-C-O C=O	O=C=O	O=C	C _{arom.} -O-C
At% exp.	63	16	13	2	6	32	68
At% theor.	63	19	12	0	6	33	67

Table 1 Relative amounts of different carbon and oxygen species obtained from the deconvolution of the C1s and O1s core level spectra (see Fig. 2), compared with the theoretical composition of PC.

Figure Captions

Figure 1 Monomeric unit of the polymeric structure of PC. The numbers correspond to specific chemical species of carbon and oxygen, present in the molecule: 1) aromatic carbon, 2) aliphatic carbon, 3) C-O, 4) O=C=O, i) O=C and ii) C-O-C.

Figure 2 XPS C1s (a) and O1s (b) detail spectra of a 3 nm layer of PC evaporated on Au(111). The deconvolution of the carbon 1s and oxygen 1s core level spectra is in good agreement with the chemical composition of the polymer. The additional peak (*) might originate from chemical modifications of some of the carboxyl groups (black: original data, green: fitted species, red: entire fit).

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3 Figure 3 UPS He I valence band spectra of the PC-Au(111) interface as a function of PC
4 coverage. The dashed spectrum represents a clean Au(111) surface. The
5 positions of characteristic valence band emissions of the substrate (I-VI) and of
6 the polymer (A-G) are indicated.
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12 Figure 4 RT-STM images of a sub-monolayer coverage of PC evaporated on Au(111),
13 showing the formation of small islands with a chain-like structure ($I_t = 0.1$
14 nA, $V_t = -1$ V). a) The herringbone reconstruction of a clean Au(111) surface
15 is still visible (*), indicating that there is no strong interaction between the
16 adsorbate and the substrate. Inset: the clean Au(111) surface. b) Indication of
17 the island orientation (with respect to the scan direction): there seems to be
18 no preferential orientation of the islands either to the herringbone
19 superstructure or to step edges.
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28 Figure 5 High resolution RT-STM images of the adsorbate islands ($I_t = 0.1$ nA, $V_t = -1$
29 V). Depending on the scan direction with respect to the island orientation, the
30 molecular structures appear different. In the case of scanning along the
31 chain-like protrusions, which appear for large scale images a), the islands
32 exhibit a periodic and complex arrangement of distinctive molecular features
33 b). Scanning more perpendicularly to the chain-like arrangement c), offers a
34 slightly different insight into the molecular structure, which now seems to be
35 more complex, but showing the same periodicity d).
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44 Figure 6 Proposed and simplified model of the molecular arrangement of PC oligomers,
45 overlaid on the STM image of Figure 5 b) and d).
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49 Figure 7 Dissociation energies of specific bonding species within the PC molecule.
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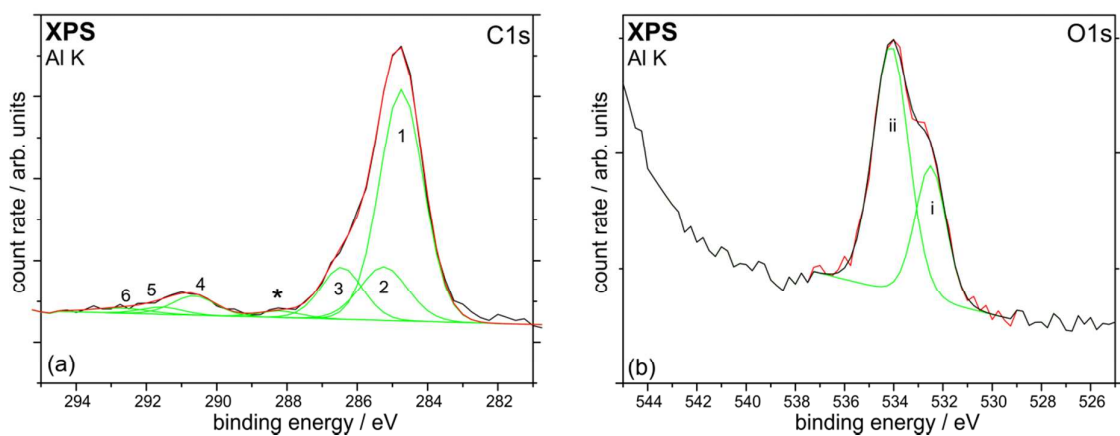
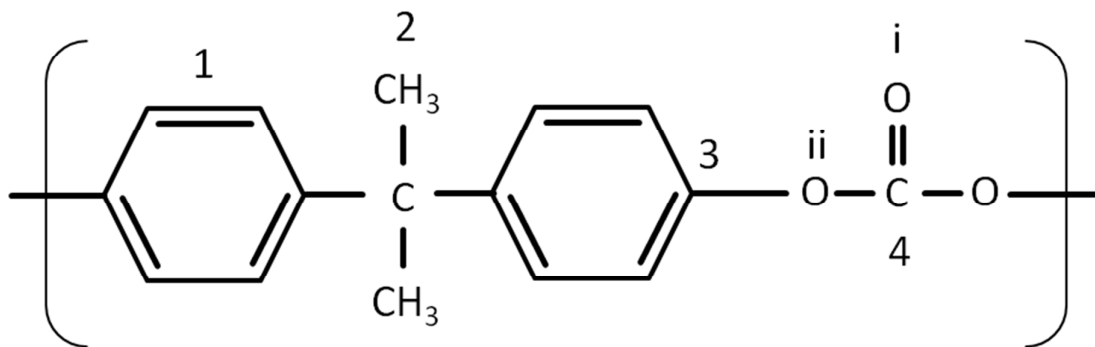


Figure 2

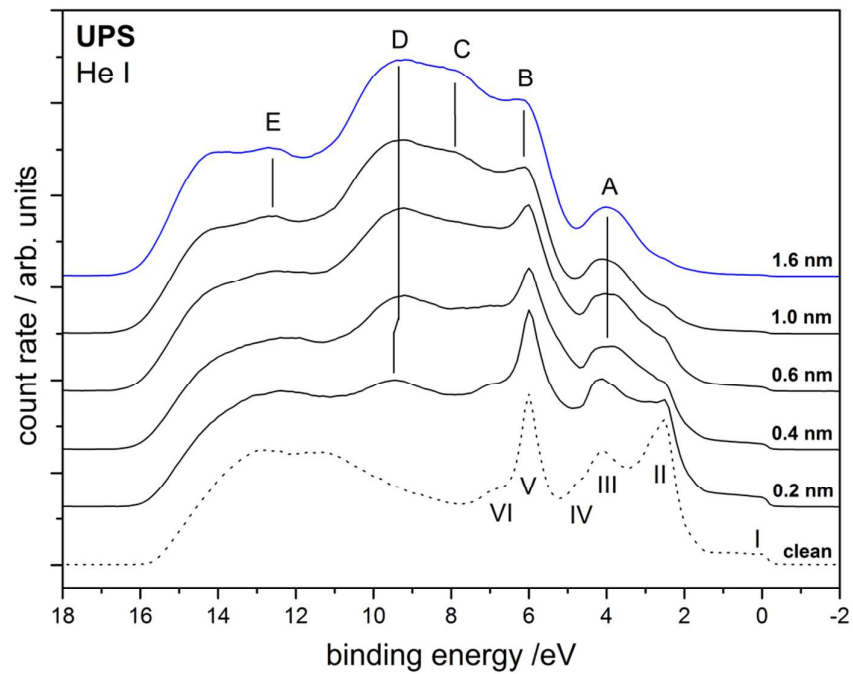


Figure 3

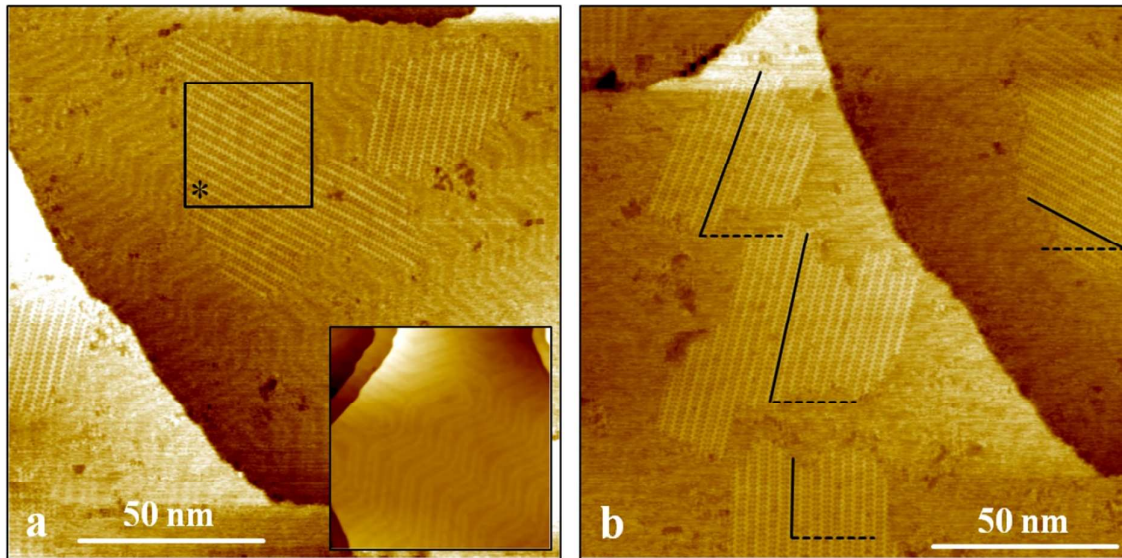


Figure 4

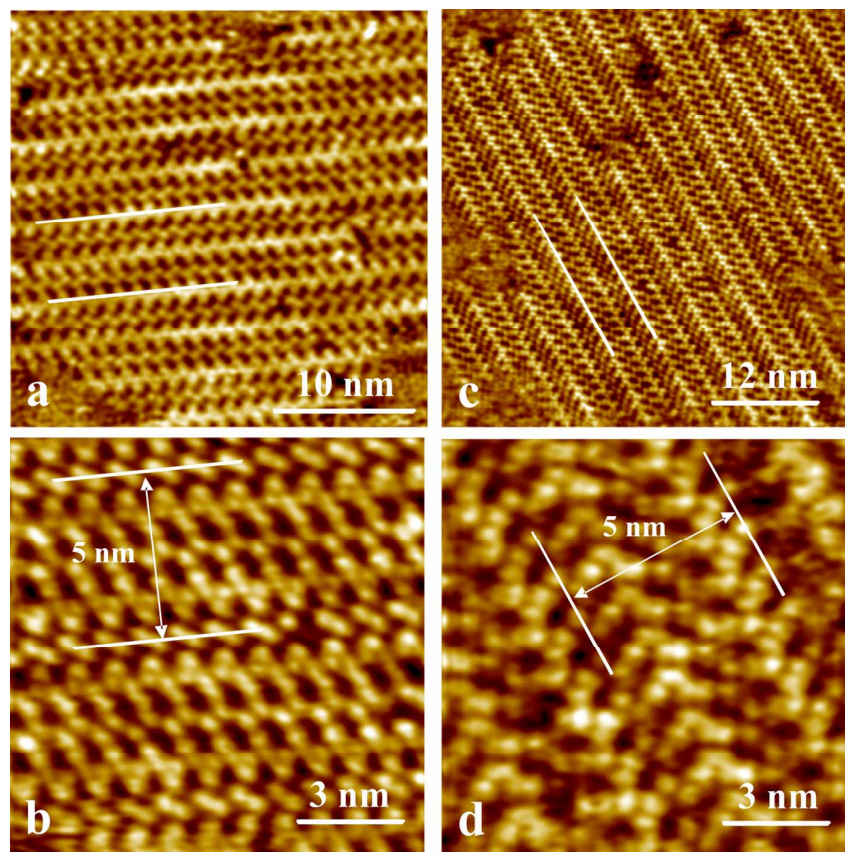


Figure 5

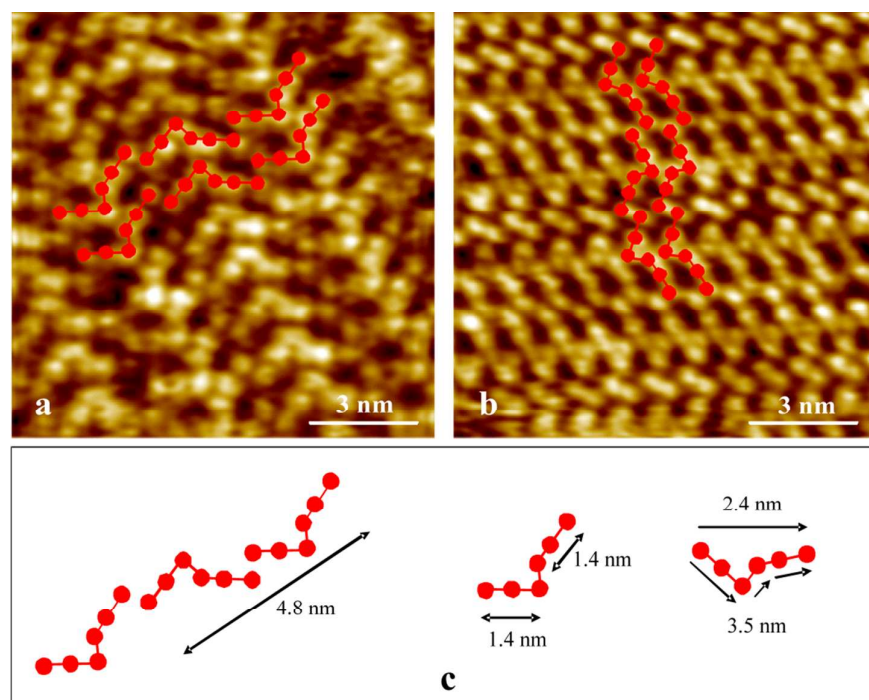


Figure 6

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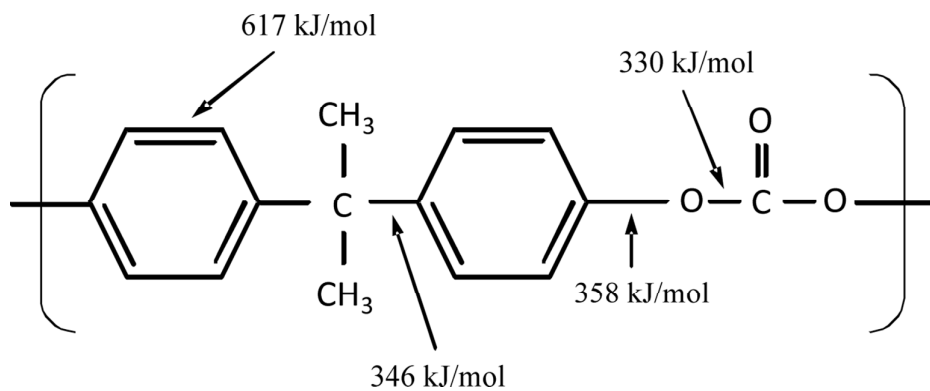
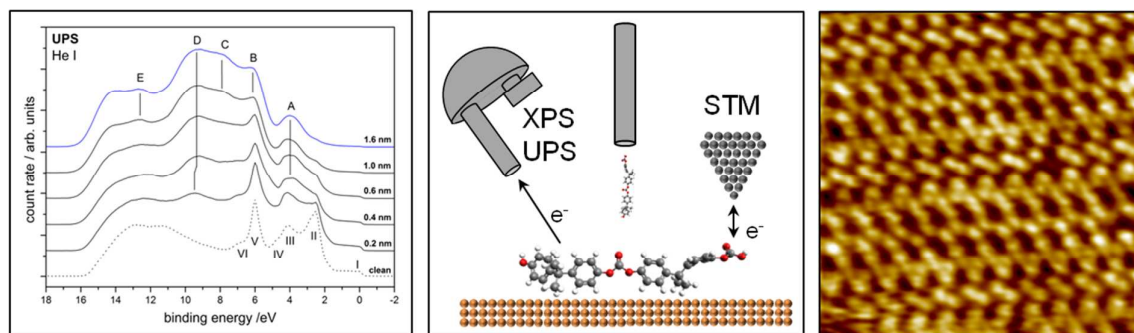


Figure 7

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